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DESCRIPTION

METHOD OF PRODUCING HEAT-RESISTANT FLEXIBLE LAMINATE

TECHNICAL FIELD

5 The present invention relates to a method of producing a laminate, which comprises continuously laminating a heat-resistant film having thermal fusibility with a metallic foil. More particularly, the present invention relates to a method of producing a laminate for use in the production  
10 of electronic and electric equipments.

BACKGROUND ART

Laminates for use in the formation of printed circuit boards for electronic and electric equipments includes, for  
15 example, laminates comprising metallic foils bonded with a thermosetting adhesive made of a thermosetting resin (hereinafter referred to as thermosetting laminates) and laminates comprising metallic foils bonded with a thermally fusible adhesive made of a thermoplastic resin (hereinafter referred to as thermally fusible laminates).

Various methods of producing thermosetting laminates have hitherto been studied. Examples thereof include a method of pressing a resin-impregnated paper or glass cloth with metallic foils, using a multistage press or a vacuum press  
25 and then thermally curing the resin at high temperature for

several hours to obtain a rigid laminate, a method of laminating a roll-shaped material while being interposed between a pair of heated roll laminating apparatuses (thermal laminating apparatuses) and then thermally curing the material at high 5 temperature for several hours to obtain a rigid laminate, and a method of thermally laminating using a double-belt press in place of the thermal laminating apparatus.

These thermosetting laminates are usually produced by forming under pressure at a temperature of 200°C or lower. 10 Small thermal stress is applied on a laminating material at such a low heating temperature, and therefore less adverse influence is exerted on appearance of the laminates.

On the other hand, in the production of the thermally fusible laminates, thermal fusion can not be achieved under 15 pressure unless the heating temperature is higher than a glass transition temperature (Tg) of a thermoplastic resin constituting a bonding layer. Since the laminates for electronic and electric equipments are heated to high temperature in the process of packaging of parts, Tg of at 20 least 180°C is required to the thermoplastic resin constituting the bonding layer. Furthermore, thermal fusion of the resin requires thermal lamination at a temperature of not lower than 200°C. For example, aforementioned 25 descriptions are disclosed in Japanese Unexamined Patent Publication (Kokai) No. 4-33848, Japanese Unexamined Patent

Publication (Kokai) No. 11-300887, Japanese Patent No. 2652325,  
and Japanese Unexamined Patent Publication (Kokai) No.  
9-116254.

Since these laminates are exposed to high temperature  
5 in the lamination process and may be adversely affected by  
various forces, there arises a so-called "end waviness"  
phenomenon wherein the ends of the resulting laminate are in  
a wavy state. End waviness wherein the ends of the laminate  
are not in a flat state causes such a problem that the laminate  
10 can not be satisfactorily fixed by evacuation from the back  
side of the laminate to cause pattern deviation when a circuit  
pattern is formed by applying a photoresist on the laminate,  
followed by exposure, development and further copper foil  
etching.

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#### DISCLOSURE OF THE INVENTION

An object of the present invention is to solve such  
a problem that pattern deviation may be caused by end waviness  
of the heat-resistant flexible laminate in the process for  
20 formation of a circuit and to provide a heat-resistant flexible  
laminate having good appearance.

A mechanism for production of end waviness is not sure,  
but is considered as follows. In the cooling process after  
laminating the laminating materials at high temperature under  
25 pressure, the temperature of the ends decreases prior to the

center portion to cause a difference in temperature between the ends and center portion. Since the amount of contraction of the laminate varies with the temperature, the ends contract drastically as compared with the center portion. In case the 5 laminate is continuously produced, a force of taking up the laminate, i.e. take-up tension is applied to the laminate. In case the take-up tension is applied in the cooling process in the state where the ends contract drastically as compared with the center portion, the ends are extended to cause plastic 10 deformation. When cooled to normal temperature, the ends are loosened as a result of plastic deformation, and thus there arises a so-called "end waviness" phenomenon wherein the ends of the laminate are in a wavy state.

The present inventors have intensively studied about 15 a method of controlling end waviness of the laminate and, as a result, the present invention has been completed.

The present invention is directed to a method of producing a laminate, which comprises continuously laminating a heat-resistant film having thermal fusibility with a 20 metallic foil, characterized in that the temperature of the ends of the laminate is the same as or higher than that of the center portion in the cooling process after lamination.

In preferable embodiment, the present invention is directed to aforementioned method, wherein the temperature 25 of the ends is 40°C higher than that of the center portion.

In more preferable embodiment, the present invention is directed to any one of aforementioned methods, which comprises laminating using a heated roll laminating apparatus.

In more preferable embodiment, the present invention 5 is directed to any one of aforementioned methods, which comprises disposing a protective material between the pressing surface of the heated roll laminating apparatus and a laminating material, thermally laminating them at 200°C or higher, thereby to slightly contact the protective material 10 with the laminating material, cooling the laminate and removing the protective material from the laminate.

In more preferable embodiment, the present invention is directed to any one of aforementioned methods, wherein the 15 heat-resistant film having thermal fusibility comprises a non-thermoplastic polyimide film and a resin containing a thermally fusible component provided on the surface of the non-thermoplastic polyimide film.

In more preferable embodiment, the present invention is directed to any one of aforementioned methods, wherein the 20 thermally fusible component of the heat-resistant film contains a thermoplastic polyimide in an amount of 50% by weight or more based on 100% by weight of the thermally fusible component.

In more preferable embodiment, the present invention 25 is directed to any one of aforementioned methods, wherein the

metallic foil is a copper foil having a thickness of 50  $\mu\text{m}$  or less.

In more preferable embodiment, the present invention is directed to any one of aforementioned methods, wherein the 5 protective material is a non-thermoplastic polyimide film.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing a thermal laminating apparatus.

10 Fig. 2 is a schematic diagram showing a heater for controlling end waviness.

Fig. 3 is a diagram showing a state of waviness.

#### Brief Description of the Reference Symbols

1: Copper foil

15 2: Heat-resistant film having thermal fusibility

3: Protective material

4: Heated roll laminating apparatus

5: Protective material take-up apparatus

6: Product take-up apparatus

20 7: Heater for controlling end waviness

8: Far infrared heater

9: Sample

#### BEST MODE FOR CARRYING OUT THE INVENTION

25 The present invention will now be described in detail.

The laminate obtained by the method of the present invention can be preferably used as a flexible laminate for electronic and electric equipments, though applications thereof are not specifically limited.

5 Examples of the heat-resistant film having thermal fusibility in the present invention include a single-layer film made of a resin having thermal fusibility, a multi-layer film comprising a core layer having no thermal fusibility and a resin layer having thermal fusibility formed on either or 10 both sides of the core layer, and a film comprising a base material made of paper or glass cloth impregnated with a resin having thermal fusibility. Since the resulting film is inferior in flexibility when using a base material having 15 rigidity such as glass cloth, the film for heat-resistant flexible laminate is particularly preferably a single-layer film made of a resin having thermal fusibility, or a multi-layer film comprising a core layer having no thermal fusibility and a resin layer having thermal fusibility formed on either or both sides of the core layer.

20 The term "thermal fusibility" as used herein means a property wherein elastic modulus of the film is lowered by heating to the temperature of higher than a glass transition temperature (Tg), thus making it possible to laminate with a laminating material. The term "heat resistance" as used 25 herein means a property capable of enduring continuous duty

at the temperature of not lower than 200°C.

Examples of the resin having thermal fusibility include polyethylene, polystyrene, polypropylene, polyester, poly(meth)acrylate, and thermoplastic polyimide. Among 5 these resins, resins containing a thermoplastic polyimide component, for example, thermoplastic polyamideimide, thermoplastic polyether imide, thermoplastic polyester imide or the like can be preferably used in view of heat resistance. The content of the thermoplastic polyimide is preferably 50% 10 by weight or more, and more preferably 70% by weight or more, based on 100% by weight of the thermal fusibility component. To improve adhesion, the thermal fusibility component may contain a thermosetting resin such as epoxy resin, phenol resin, or an acrylic resin having a reactive group. To improve 15 various properties, the thermally fusible component may contain various additives.

The heat-resistant film having thermal fusibility in the present invention is not specifically limited as long as it has a heat-resistant and thermally fusible resin layer as 20 an outermost layer. For example, the heat-resistant film may be a single-layer composed only of a thermally fusible resin, but is preferably a three-layer structure film comprising a core layer having no thermal fusibility and a resin layer having thermal fusibility provided on both sides of the core layer 25 in view of dimensional stability. A two-layer structure film

comprising a core layer having no thermal fusibility and a resin layer having thermal fusibility provided on one side of the core layer can also be used. In case of the two-layer structure film, no thermally fusible layer is preferably provided on the side, on which a thermally fusible layer is not provided, in order to prevent warp after laminating a metallic foil.

5 The core layer having no thermal fusibility is not specifically limited as long as it has heat resistance and 10 examples thereof include non-thermoplastic polyimide film, aramid film, polyether ether ketone film, polyether sulfone film, polyallylate film, and polyethylene naphthalate film. Among these films, a non-thermoplastic polyimide film is preferable in view of electrical characteristic.

15 Preferable examples of the heat-resistant film in the present invention include a film comprising a non-thermoplastic polyimide film and a layer made of thermoplastic polyimide provided on either or both sides of the non-thermoplastic polyimide film.

20 The method of forming the heat-resistant film having thermal fusibility in the present invention is not specifically limited. In case the heat-resistant film is a single-layer film containing a resin having thermal fusibility, a film can be formed by a belt-cast method or an extrusion 25 method. In case the heat-resistant film having thermal

fusibility comprises three layers of a thermally fusible layer, a core layer having no thermal fusibility and a thermally fusible layer, there can be used a method of applying a resin having thermal fusibility on both sides of a core layer having 5 no thermal fusibility (for example, heat-resistant film) separately or simultaneously to form a three-layer film, and a method of laminating a resin layer having thermal fusibility on both sides of a heat-resistant film to form a three-layer film. In the method of forming a three-layer film by applying 10 a resin having thermal fusibility, when using thermoplastic polyimide as a thermally fusible component, there can be used a method of applying a resin in a state of polyamic acid as a precursor on a heat-resistant film and imidating the polyamic acid while drying, and a method of directly applying a soluble 15 polyimide resin and drying the resin, and a method of forming a thermally fusible layer is not specifically limited. In addition to these methods, there is a method of simultaneously extruding a resin for thermally fusible layer, a resin for core layer having no thermal fusibility and a resin for 20 thermally fusible layer to form a heat-resistant film having thermal fusibility.

Examples of the metallic foil in the present invention include, but are not limited to, copper foil, aluminum foil, and SUS foil. Among these metallic foils, a copper foil is 25 preferable used in view of conductivity and cost in case of

a laminate for use in the production of electronic and electric equipments. The thickness of the copper foil is preferably 50  $\mu\text{m}$  or less because smaller line width of a circuit pattern can be achieved as the thickness of the copper foil decreases.

5 Since the copper foil having a thickness of 18  $\mu\text{m}$  or less is less elastic than the copper foil having a greater thickness and wrinkles may be produced during thermal lamination. Therefore, the present invention exerts a remarkable effect when using a copper foil having a thickness of 18  $\mu\text{m}$  or less.

10 Examples of the copper foil include, but are not limited to, rolled copper foil and electrolytic copper foil. The surface of these copper foils may be coated with an adhesive made of a resin having thermal fusibility.

In the present invention, the apparatus for continuously laminating the heat-resistant film having thermal fusibility with the metallic foil is not specifically limited as long as it is an apparatus capable of thermally pressuring, and examples thereof include single-action press, vacuum press, autoclave apparatus, heated roll laminating apparatus, and double-belt press. Among these apparatuses, heated roll laminating apparatus and double-belt press are preferable because they are suited for continuous production. As compared with batch production, continuous production enables an improvement in productivity and a reduction of loss.

25 The heated roll laminating apparatus is not

specifically limited as long as it is an apparatus for thermally pressurizing laminating materials. Heating method is not specifically limited as long as it can heat at a predetermined temperature and examples thereof include heating medium 5 circulating system, hot-air heating system, and dielectric heating system. The heating temperature is preferably 200°C or higher. When used for application wherein a laminate is passed through a solder reflow furnace at an atmospheric temperature of 240°C for the purpose of packaging electronic 10 parts, the heating temperature is 240°C or higher because a heat-resistant film containing a thermally fusible component having predetermined Tg is used. Examples of the material of the press roll include, but are not limited to, rubber and metal. In case the lamination temperature reaches high 15 temperature such as 280°C or higher, the rubber roll can not be used because the rubber deteriorates. In such a case, a metal roll is preferably used. The pressuring system is not specifically limited as long as it can apply a predetermined pressure, and examples thereof include oil hydraulic system, 20 pneumatic system, and pressure system between gaps. The pressure is not specifically limited.

The protective material in the present invention is not specifically limited as long as it can play a role of preventing poor appearance such as wrinkles of the laminate 25 product and examples thereof include paper, metallic foil,

and plastic film. Among these materials, a plastic film is preferable in view of utility and cost. Furthermore, heat-resistant films such as non-thermoplastic polyimide film, aramid film, polyether ether ketone film, polyether sulfone film, polyallylate film, or polyethylene naphthalate film are preferable because they endure the temperature upon processing. In case of processing at 250°C, a heat-resistant film having more excellent heat resistance must be used and therefore a non-thermoplastic polyimide film is preferable.

The thickness of the protective material is not specifically limited, but is preferably 50 µm or more for the purpose of suppressing the formation of wrinkles of the laminate. The thickness of the protective material is more preferably 75 µm or more because the formation of wrinkles can be suppressed almost completely. The protective material is not necessarily subjected to a surface treatment as long as it slightly contacts with the laminating material, but may be optionally subjected to the surface treatment in order to suppress adhesion. As long as the surface treatment enables the protective material to slightly contact with the laminating material, the surface treatment may be applied for other purposes, for example, rust prevention treatment applied for the purpose of preventing oxidation of the surface. The state of slight contact as used herein means a state where the protective film and the laminating material are not

mutually peeled off when any force is not applied, but they can be mutually peeled off by hands with ease.

The present invention is characterized in that the temperature of the ends of the laminate is the same as or higher than that of the center portion in the cooling process after lamination. The temperature of the center portion and the ends can be controlled by a system having a mechanism capable of controlling the temperature of the center portion and the ends without any limitation. Examples thereof include heater system capable of controlling the temperature in a width direction, heated roll system, and heating oven system. The heater is not specifically limited as long as it can controlled to a predetermined temperature, and either far infrared heater or near infrared heater can be used.

The preset temperature of the heater is appropriately controlled by the distance from the laminate and intervals, and the surface temperature of the laminate is controlled within a range from 130°C to lamination temperature, preferably from 150°C to (lamination temperature - 50°C), and more preferably from 180°C to (lamination temperature - 100°C). When the surface temperature of the laminate is lower than the above range, contraction due to air cooling after lamination can not be reduced and the waviness-control effect may not be exerted. To the contrary, when the surface temperature is higher than the above range, the bonding layer

reduces its elasticity, and thus adverse influence of the take-up tension may be exerted to cause plastic deformation, resulting in poor appearance. The surface temperature of the laminate can be measured by a thermocouple or a contact 5 thermometer.

In view of the end waviness-control effect, difference in temperature between the center portion and the ends is preferably 40°C or higher, and more preferably 60°C or higher. When the difference in temperature is smaller than the above 10 range, contraction of the ends may not be sufficiently reduced and the waviness-control effect may not be exerted.

Upper limit of the difference in temperature is preferably 150°C, and more preferably 120°C. When the upper limit of the difference in temperature exceeds the above value, 15 the laminate is heated beyond heating required to compensate temperature drop of the ends. Therefore, the temperature of the center portion decreases and waviness may occur in the center portion of the laminate.

The present invention will be described in detail by 20 way of examples, although the present invention is not limited to these examples in any sense.

#### EXAMPLES

Glass transition temperature (Tg) in the Examples was measured in a nitrogen gas flow under the conditions of a heating 25 rate of 10°C/min and a temperature within a range from room

temperature to 400°C using DSC CELL SCC-41 manufactured by Shimadzu Corporation (differential scanning calorimetry). A thermal lamination apparatus with the configuration shown in Fig. 1 was used. To control the temperature in a width direction in the cooling process after lamination, a commercially available infrared heater was arranged to control the temperature of the ends and center portion of samples (see Fig. 2).

As shown in Fig. 3, the degree of end waviness was expressed by the width W (mm) of waviness and the height d (mm) of waviness. Degree of end waviness of samples was rated by the following criteria.

- ◎ (Excellent): width (W) of waviness is 0
- (Good): W is larger than 0 and smaller than 30 mm
- △ (Ordinary): W is larger than 30 mm and smaller than 60 mm
- × (Poor): W is larger than 60 mm

(Examples 1 to 3)

Each of flexible laminates was produced by disposing a three-layer structure film having a thickness of 25 µm and a width of 260 mm (PIXEO BP HC-142, manufactured by Kaneka Corporation) containing a thermoplastic polyimide resin component having Tg of 240°C on both sides of a non-thermoplastic polyimide film, disposing a 18 µm thick electrolytic copper foil (3EC-VLP, manufactured by Mitsui Metal Industrial Corp.) on both sides thereof, disposing a

125  $\mu\text{m}$  thick polyimide film (APIKAL 125NPI, manufactured by Kaneka Corporation), as a protective film, on both sides thereof, laminating them under the conditions of a pass line shown in Fig. 1, a temperature of 380°C, a linear velocity 5 of 2.0 m/min and a lamination pressure of 200 N/cm using a heated roll laminating apparatus, cooling to normal temperature in the state where the protective film slightly contacts with the flexible laminate, and removing the protective film from the flexible laminate. The conditions 10 of difference in temperature between the ends and center portion of the laminate are shown in Table 1. The resulting flexible laminates have less waviness at the ends and good appearance.

(Comparative Examples 1 and 2)

15 In the same manner as in Examples 1 to 3, except for the conditions of difference in temperature shown in Table 1, flexible laminates were produced. The resulting flexible laminates exhibited large end waviness and poor appearance.

Table 1

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
(Temperature of ends) - (Temperature of center portion)	°C 60	40	20	-20	-40
Degree of end waviness	◎	○	△	×	×
Width of waviness (W)	mm 0	20	40	100	120
Height of waviness (d)	mm 0	1	1	4-6	5-7

## INDUSTRIAL APPLICABILITY

The laminate obtained by the method of producing a laminate of the present invention has good appearance and controlled end waviness. Thus, it is made possible to provide  
5 a heat-resistant flexible laminate which is particularly suited for use in the production of electronic and electric equipments.